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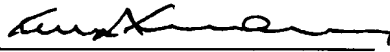
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For: Photovoltaic Solar Cell...

English Translation of the Instant International Application as Filed

Translator's Certificate of Accuracy

I, Karl Hormann, being fully conversant in the English and German languages, hereby certify that the attached is a correct and accurate translation of the International Application as originally filed in the German language.



Karl Hormann
9 April 2006

Photovoltaic Solar Cell with Metal Nano Emitters and
Method of Its Manufacture

5 Specification

The invention relates to a photovoltaic solar cell with an electrical solid material contact between a semiconductor layer of a layer thickness of d_{HL} and with a plurality of metal nano emitters embedded in an electrically
10 insulating oxide layer disposed on the semiconductor layer and each provided with a space-charge region of dimension w within the semiconductor layer to which the minority carriers migrate over a diffusion length L , and with a transparent conductive layer electrically insulated from the semiconductor layer by the oxide layer as well as with front and rear contacts, and to a
15 method of manufacturing such a solar cell.

In photovoltaic current generation the efficiency of the conversion of impinging sun light to electrical current is of the utmost importance. In order to obtain an optimum yield, aside from reducing losses of reflection and
20 recombination, particular efforts are made to reduce losses from shadows on the light irradiation surface and to improve the collection of light. Shadows on the light irradiation surface result especially from the front contacts, the transparent electrically conductive layer, for instance ITO, and from the emitter layer in the case of Schottky-type solar cells with a solid material
25 contact between the doped semiconductor layer and a rectifying metal layer. The same is true of simple p-n-transitions between a normally doped and a highly doped semiconductor layer. For purposes of an efficient photovoltaic conversion of energy between solid material contacts the emitter layer may be applied as a very thin uninterrupted layer on the semiconductor layer
30 operating as the base or absorber. This may be done by vacuum processes, such as PVD, and diffusion processes. Furthermore, dot-contact solar cells

have been proposed which on their rear surface are provided with an optimized dot-contact pattern in direct contact with highly doped insertion zones in the absorber layer (see publication I by J. Zhao et al.: "22.7% efficient pearl silicon solar cell module with a textured front surface", 26th PVSC, 1197, Anaheim, CA, pp. 1133-1136, Fig. 2). From this publication, pyramidal structuring of the cell surface in the region of the uppermost layers, including the emitter layer, for the prevention of reflections, are also known. However, in the area of the of this surface structuring the depth of penetration of the emitter layer into the semiconductor layer of correspondingly conforming structure is relatively minor. The front contacts are applied as strips as narrow as possible in order to reduce losses from shadows and thus to increase the conversion efficiency of the solar cell. The emitter layer is applied as a closed surface and is more highly doped beneath the contact strips than in the area of directly impinging sunlight. Furthermore, for purposes of reducing shadow losses it is known from WO 02/103810 A1 to structure the front contact as wedge-like troughs which are narrower than simple contact strips but which have a greater depth of penetration into the emitter layer and the semiconductor layer positioned below it (buried contact). However, no significant improvement in efficiency can be achieved in view of the fact that the main light collection takes place in the area of the contact-free emitter-absorber transition with increased depth of penetration. For improving the efficiency, it is known from Japanese abstract JP 04015963 A to insert individual emitter regions deeply into the absorber layer in order to prevent recombinations (buried insular regions). However, each emitter region is connected to a front contact strip by its own contact hole. A similar approach of the semiconductor material is known from DE 198 37 365 A1 which teaches the insertion of clusters into the active absorber layer for providing additional charge carriers. For using additional wavelength ranges of the sunlight this leads to changing the optical properties of the semiconductor. However, the clusters grow with inherent defects and are thus difficult to control in terms of their distribution and size.

The state of the art upon which the present invention is based, is disclosed by Publication II by H. Tsubomura et al.: "Effect of Microscopic Discontinuity of Metal Overlayers on the Photovoltages in Metal-Coated Semiconductor-Liquid Junction Photoelectrochemical Cells for Efficient Solar Energy Conversion". This publication aims primarily at improving the catalysis of the photo-chemical process in an electrolytic solar cell (PEC). The application of catalytically active metal films resulted in a solid material contact which, structured as a Schottky contact, is necessarily inferior to a p/n semiconductor contact since it leads to increased losses from charge carrier recombination. The quantity of the current losses occurring at the semiconductor-metal-contact may, however, be reduced by replacement of the continuous metal film by very small (diameter in the range of several nm) metal islands as metallic nano emitters which cover but a small portion of the surface. These metal dot contacts are fabricated by etching of a metal film on a silicon diode. However, in an aqueous electrolyte the latter immediately forms an oxidic insulating layer. In this manner, the semiconductor-electrolyte-contact is replaced by a pure solid material contact in which in addition to catalytically active metal islands an insulating oxide layer covers most of the surface. In discussing his publication, Tsubomura states that his approach of reducing current losses can be applied to a solid material solar cell if instead of the redox electrolytic solution a transparent conductive layer is applied to the oxide layer. However, Tsubomura makes no statements relating to dimensional rules regarding size and distribution of the metal islands. The islands are disposed on the surface of the semiconductor layer at a relatively large distance from each other (four times their diameter), so that the efficiency attainable particularly in solid material solar cells is not fully satisfactory.

Accordingly, the object of the invention is to be seen as so further to improve the photovoltaic solar cell described *supra* that a further improvement in the efficiency of the photovoltaic energy conversion can be achieved with

structure. Furthermore, they may extend obliquely within the semiconductor layer so that all regions of the layer may be optimally reached by the nano emitters. Thus, in the solar cell in accordance with the invention, the entire layer thickness of the absorbing semiconductor layer up to the rear contact
5 may be used for energy conversion thus yielding optimum efficiency in the collection of the light-generated minority carriers while avoiding recombination effects. Dotted nano emitters can only achieve a depth of penetration as a function of the simple length of diffusion so that for taking up the entire absorbing semiconductor layer it must be structured corresponding-ly thin.

10 On the other hand, for light collection of approximately 90% the layer thickness of the semiconductor layer has to be greater than three times the absorption length $1/\alpha$ with the coefficient of absorption α which may lead to overlapping marginal conditions and attendant lower efficiency.

15 In consequence of the penetration into the depth of the absorbing semiconductor layer, the invention makes possible the use of semiconductor materials which are not of first class quality, i.e. materials of lesser diffusion length of the minority carriers. This results in a noticeable cost reduction. Furthermore, crystalline materials and epitaxially grown layers of, for instance,
20 Si, GaAs and InP may be made significantly thinner in view of the fact that in the solar cell in accordance with the invention the red sensitivity in the collection near the rear contact is significantly improved. This is particularly true if, in accordance with one embodiment of the invention a reflective layer is applied to the rear surface of the semiconductor layer in front of the rear
25 contact. According to a further embodiment of the invention a further improvement of the conversion efficiency results from applying an antireflection coating to the transparent conductive layer. This may be, for instance, a layer with a positive or negative pyramidal structure or with some other micro-structuring which safely catches impinging light and conducts it to
30 the absorber.

two solid material contacts. In this connection, a preferred method of fabricating such a highly efficient solid-material solar cell is to be economical and energy conserving.

5 In the accomplishment of this object there is thus provided in a solar cell of the kind referred to with an electrical solid material contact between a semiconductor layer of a d_{HL} layer thickness and a plurality of metal nano emitters each having a space-charge region of a dimension w in the semiconductor to which the minority carriers in the semiconductor migrate
10 over a diffusion length L , that the metallic nano emitters are of acicular or rib-like structure and are disposed at a uniform space $D \leq \sqrt{2}L$ from each other as well as a depth of penetration $T \geq d_{HL} - \frac{L}{2} + w$ into the semiconductor layer.

 In the solid material solar cell metal nano emitters are used with a
15 predetermined homogenous density distribution dependent upon the occurring minority carriers or their length of diffusion in the semiconductor, thus ensuring minimum use of material at an optimum freedom from shadows of the absorbing semiconductor layer by the second solid material contact and minimum recombination losses. Thus a high conversion efficiency can
20 be achieved in the current collection. In accordance with the invention, the current collection is further significantly improved by the metal nano emitters being now structured three-dimensionally in an acicular or rib-like manner and penetrating deeply into the semiconductor layer. By contrast, the metal nano emitters of the prior art are two-dimensionally structured in a dotted fashion
25 and are present only at the surface of the absorbing semiconductor. Also, the depth of penetration of the metal nano emitters in accordance with the invention can be precisely calculated as a function of the relevant parameters of length of diffusion L , space charge zone w and layer thickness d_{HL} of the semiconductor layer, and can thus be optimized. In accordance with an
30 advantageous embodiment of the invention the metal nano emitters in the semiconductor layer may have lateral branches thus resulting in a tree-like

The use of metal for the nano emitter results in a Schottky contact. The metal must be selected such that it forms a rectifying contact. Thus, for p-doped semiconductor material a metal of a low work function and for n-doped semiconductor material a metal of a higher work function must be selected. Schottky solar cells offer the advantage that they form a diode contact simply by applying a metal to the semiconductor layer. There is no need for complex and complicated doping processes and stability tests at differently doped areas. It should, however, to be noted at this point that the nano emitters may also consist of semiconductor material. The use of a highly doped semiconductor material as a nano emitter results in an efficient p-n-transition provided the semiconductor materials are correspondingly doped in an opposite manner. In accordance with the invention, the shadowing of the absorbing semiconductor layer and the use of material may be kept particularly low by a size of nano emitters in the nm range (preferably between 10 nm and 100 nm). However, dimensions of nano emitters down to the μm range are possible as well. The nano emitters may be grown directly on the semiconductor layer, or they may be applied as a colloid. On the semiconductor layer, they are surrounded by the oxide layer and may slightly extend beyond it. Thus the nano emitters may extend into the transparent conductive layer applied to the oxide layer. The absorbing semiconductor may, but need not, be doped (p- or n-doped). Though extremely pure, so-called float zone (FZ), silicon is nominally undoped, yet it is slightly n-conductive. It is used for high-efficiency solar cells. So-called "Czochralski (CZ) silicon does not reach the quality of FZ silicon so that it requires doping. The oxide layer may be a native oxide such as, for instance, SiO_2 which is anodically grown by an exposure or application of a potential. Further details regarding the structure may be taken from the description of possible methods of fabrication set forth *infra*.

It is also an object of the invention to provide a method of fabricating a photovoltaic solar cell having the claimed structure and which is cost-efficient

and requires low energy consumption. In a preferred method, this object is accomplished by the following process steps:

- 5 ● wet-chemical or electrochemical or photo-electrochemical application of an electrically insulating oxide layer of high electronic quality on a semiconductor layer;
- structuring the oxide layer by dotted or linear removal of the oxide layer at the locations provided for applying the nano emitters;
- wet-chemical or electrochemical or photo-electrochemical acicular or rib-like etching of the structure in the oxide layer down into the
10 semiconductor layer;
- light-induced or potential-controlled electrochemical precipitation from a redox electrolyte of metal into the structure in the oxide layer and into the semiconductor layer;
- wet-chemical or electrochemical or photo-electrochemical application
15 of a transparent conductive layer on the oxide layer; and
- application of front and rear contacts.

In accordance with a preferred embodiment the oxide layer may be structured by a wet-chemical or electrochemical or photo-electrical process so
20 that the fabrication process of the solar cell may be continuously performed wet-chemically or electrochemically or photo-electrochemically in a range of low temperatures. The application of the front contacts, for instance contact blades, being normally carried out by vapor deposition, is excluded from this. This is, however, a standardized process which does not increase either the
25 complexity or costs of the process. On the other hand, the fabrication is significantly affected by the process parameters. In this context, the invention, by avoiding high temperatures and changing processes, may yield a significant improvement in the process. The wet-chemical / electrochemical processes may be scaled slightly upwardly and may be used for producing
30 large surfaces as is well-known from galvanic processes.

Precise positioning and maintaining the dimensions of the nano emitters by precisely structuring the oxide layer and the semiconductor layer are important as regards improving the efficiency of the solar cell with specially structured metal nano emitters described *supra*. In technological applications, the oxide layer may be structured, for instance, by electron beam lithography or by ion beam etching (FIB = focused ion beam etching). Alternatively, but still without applying high temperatures, the oxide layer, which may consist of ZnO, SnO₂ or ITO, may be structured, in accordance with a further embodiment of the process, by scanning probe microscopy which would result in a still more precise and controlled definition of the nano emitter positions. In this context, two basic possibilities exist: On the one hand the oxide layer may be scanned in a selected surface area by AFM (atomic force microscopy) with a sufficiently high hold-down force. This process results in the oxide layer being correspondingly shifted laterally and in the semiconductor layer disposed under it to be exposed. On the other hand it is possible by means of AFM to form an indentation with a diamond needle by which the oxide layer is penetrated for the formation of a contact. In accordance with a further embodiment of the invention it is also possible in mechanically structuring the oxide layer to provide a plurality of indentations by parallel embossing for structuring an oxide layer of large surface. By this so-called millipede technique a large number (several hundred) of indentations are simultaneously carried out by AFM (atomic force microscopy), for instance. For large-scale applications in particular such structuring is of particular interest in connection with a large-scale continuous electrochemical / wet-chemical fabrication. In order to cure deformations possibly occurring during the indenting or scratching, the structures, in accordance with a further embodiment of the method, may subsequently be subjected to careful chemical or electrochemical etching of the positions of the removed oxide layer followed by a potential, current or charge-controlled application of an electrically insulating anodic oxide layer (1 to 3 atom layers) on the structure of the semiconductor layer prior to precipitation of metal.

This process serves to suppress recombination processes at and in the vicinity of defects.

The surface structuring of the oxide layer is followed by a process step
5 for deepening the structures into the semiconductor layer. This is carried out
by wet-chemical or electrochemical or photo-electrochemical etching.
Commencing from dot structures in the oxide layer, there will result acicular or
porous recesses. Linear structures in the oxide layer are deepened to ribs or
troughs. The etching is a simple yet precise operation since the surface of
10 the semiconductor which is not to be etched is securely protected by the
oxide layer. The depth of etching may be precisely defined by the
corresponding parameters of material and time. The same is true in respect
of possible etching of lateral branches which may proceed from the central
acicular or rib-like etching recesses, as well as of recesses extending
15 obliquely within the semiconductor layer. An importance process step is the
subsequent filling of the acicular or rib-like recesses and of possible lateral
branches, i.e. the local precipitation of the metal nano emitters. In this
connection, a light-induced or potential-controlled electrochemical
precipitation of metal is carried out. The precipitation in the lateral can be
20 safely ensured. In connection with light precipitation the metal is selected
such that a rectifying Schottky contact results. The semiconductor may be p-
doped or n-doped or not be doped at all. In the case of n-semiconductors the
metal precipitation occurs in the dark by forming negative accumulation
layers. To prevent repetitions, reference is made to the specific description in
25 connection with the corresponding drawings as regards the precise operation
during the light-induced precipitation. An alternative preparation may be
carried out by introducing a metallic colloid into the acicular or rib-like
recesses in the semiconductor layer. After introduction of the colloid the
exposed surface areas of the semiconductor layer are electrochemically
30 oxidized so that the desired nano emitter structure is then embedded in an
oxide layer. Process steps following the formation of the nano emitters may

in further embodiments include the application of a reflexive layer on the rear surface of the semiconductor layer and/or the application of an antireflective layer on the transparent conductive layer. Both of these additional layers serve further to improve the efficiency as has already be set forth in
5 connection with the solar cell in accordance with the invention.

For a further understanding, embodiments of the invention will hereafter be described in greater detail with reference to the schematic drawings, in which:

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Figure 1 is a cross-sectional view of an embodiment of a solar cell in accordance with the invention;

Figure 2 is an energy band position diagram of the light-induced local precipitation of the nano emitters in the area of the nano
15 emitters;

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Figure 3 is an energy band position diagram of the light-induced local precipitation of the nano emitters in the area of the oxide layer; and

Figure 4 is a detailed view relating to the light-induced precipitation of the
20 nano emitters.

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Figure 1 depicts a photovoltaic solar cell SZ having an electrical solid material contact between a doped semiconductor layer HL of layer thickness d_{HL} and a plurality of metal nano emitters NE embedded in an electrically
25 insulating oxide layer OS on the surface of the semiconductor layer HL. Given an appropriate selection of the metal there will result a rectifying Schottky contact with the semiconductor layer HL. In the semiconductor layer HL the rectifying nano emitters NE generate a space charge zone (depleted range) of extent w . Upon exposure, provided the impinging light energy $h\nu$ is
30 greater than the work function E_g of the charge carriers, pairs of electron holes will be formed in the semiconductor layer HL. The minority carrier

(electrons for p-silicon as the semiconductor, holes or “defect electrons” for n-silicon) migrate at a diffusion length L to the metal nano emitters NE acting as a sink. A particularly efficient conversion of solar energy will be achieved if the distance D between the nano emitters NE is:

5
$$D \leq \sqrt{2}L.$$

In case of uniformity the optimum distance between the metal nano emitters NE will have been obtained which ensures minimum shadowing and minimum use of material. Where the distance D is less than an upper limit
10 there will be a corresponding overlap with an attendant higher use of material but which nevertheless ensures a safe utilization of the semiconductor layer HL in the corresponding radial plane. Where the metal nano emitters NE are exclusively disposed on the surface of the semiconductor layer HL the efficient utilization would be limited to the uppermost layer of the
15 semiconductor layer HL. In order to achieve total utilization the layer d_{HL} of the semiconductor layer HL should not be greater than the diffusion length L of a given minority carrier. In the solar cell SZ in accordance with the invention the metal nano emitters NE also extend into the depth of the semiconductor layer HL, thus resulting in the advantageous inverse case. A
20 depth of penetration $T \geq d_{HL} - \frac{L}{2} + w$ will be defined as a function of the layer thickness d_{HL} of the semiconductor layer HL, the diffusion length L of the minority carrier and the extent w of the space-charge zone. In the case of uniformity the semiconductor layer HL is optimally used down to the rear contact RK of the solar cell SZ and a safety overlap will result by going below
25 the threshold value. The layer thickness d_{HL} thus does not depend upon the absorption coefficient α or upon the absorption length $1/\alpha$ such that the layer thickness d_{HL} of the semiconductor layer would have to be greater than $3/\alpha$ in order to achieve an optimum utilization of the layer of pure crystalline semiconductor material.

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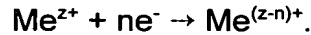
The metal nano emitters NE on the surface of the semiconductor layer

HL are surrounded by a closed oxide layer OS the layer thickness of which has to be dimensioned sufficiently thick to provide an effective insulation of the metal nano emitters NE from each other and between the semiconductor layer HL and a transparent conductive layer TCO applied to the oxide layer OS. The metal nano emitters NE may penetrate slightly into the transparent conductive layer TCO. Owing to the division of the areas between the nano emitters NE such a solar cell SZ may be called a compact solar cell. Current collection takes place by way of the front contacts FK, for instance of strip or blade form, which are applied to the transparent conductive layer TCO. Here, too, as low a shadowing as possible is to be aimed at. In order further to improve the conversion efficiency there may be provided an anti reflection layer on the upper surface and a reflective surface on the rear surface in from of the rear contact of the solar cell SZ.

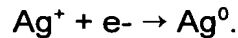
For preparing and modifying the oxide layer OS thin oxides of high electronic quality of the interface between the oxide and semiconductor layers may be wet-chemically precipitated. Further possibilities relate to fabricating anodic oxides followed by post-drying or to the use of electro-polished oxides followed by post-drying. Furthermore, thermally produced and native oxides may be used. The structuring of the oxide is preferably carried out mechanically, for instance by AFM by laterally shifting or penetrating the oxide layer OS.

For the purpose of local precipitation of nano emitters NE of metal on a semiconductor material, in this case p-Si, for forming Schottky contacts by a photo-induced electrochemical process, the energetic condition at the contact p-Si / metal / electrolyte at cathodic polarization of the silicon Si has to be taken into consideration. In this connection, a distinction is made between oxide-covered and oxide-free areas of the Si surface. The resultant light-induced processes have been depicted in energy band position diagrams (energy E over position x, E_F Fermi level). Figure 2 depicts the behavior of an

uncovered section of the semiconductor layer HL for the subsequent positioning of a metal nano emitter NE at cathodic polarization (applied voltage V_a) and exposure ($h\nu$). The light-generated excess charge carriers migrate either to the rear contact RK which in the embodiment is structured as a surface (holes (+)) or to the surface (electrons (-)). At an appropriate energetic position of the lower edge of the conductor band (E_L) and of a metal redox pair ($Me^{z+/0}$) the electrons may execute the reaction



The metallic phase develops at $n = z$. By way of simplification, the following, for instance, holds true for mono-valued metal ions:



This leads to metal precipitation, and, hence, to the formation of the metal nano emitters NE, at the free surface and depth areas of the semiconductor layer HL. The metal precipitation may also be effected at n-Si by cathodic polarization in the dark (unexposed). In that case the conductor band electrons are to be considered as accumulated majority carriers. The light-induced precipitation at p-semiconductors and precipitation in the dark on n-semiconductors at cathodic (negative) potential represent - compared to the flat band situation - a very preserving and especially well defined process compared to vapor deposition, sputtering or etching away of metal films.

Figure 3 depicts the corresponding behavior of oxide-covered areas of the semiconductor layer HL. At layer thicknesses d_{ox} of the oxide layer, which are significantly greater than the so-called tunnel thickness ($d_{ox} \geq 3 \text{ nm}$) the light-induced electrons are no longer transferred into the electrolyte. Instead, "trapping" as well as recombination occur at the adhesion positions at the surface of the semiconductor layer HL. At a sufficiently high electronic quality of the Si / oxide interface a charge carrier drift occurs in the direction of the metal nano emitters NE. This has been shown in Figure 4.

The controlled exposing of contact areas on and in the semiconductor layer HL after formation of a thicker (for instance 10 nm) anodic oxide layer OS, the subsequent precipitation of metal nano emitters NE for fabricating rectifying nano contacts and the application of SnO₂, for instance, as a transparent conductive layer TCO makes possible a continuous production of a solar cell prepared completely by a wet or electrochemical process at a low temperature. The resultant process sequence saves energy and is cost-efficient.

10 List of Reference Characters

	D	distance between nano emitters
	d _{HL}	Layer thickness of the semiconductor layer
	d _{ox}	layer thickness of the oxide layer
15	FK	front contact
	HL	semiconductor layer
	L	diffusion length of the minority carrier
	NE	nano emitter
	OS	oxide layer
20	RK	rear contact
	SZ	solar cell
	T	penetration depth of the nano emitters
	TCO	transparent conductive layer
	w	extent of the space-carrier zone

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